



Visible-light-induced aerobic oxidation of alcohols in a green catalytic system of carbonate-like species doped TiO₂



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ABSTRACT

Although all kinds of the promising catalytic approaches have been developed in recent years, pursuing a complete green catalytic system with high efficiency for the production of various aldehydes is still an interesting challenge. Moreover, the low chemo-selectivity or chemical deactivation for particular primary aldehydes with complicated substituent groups, however, is an inevitable bottleneck for achieving industrial application. Here, we construct a new green pathway in which carbonate-like species doped TiO₂ (C/T) can function as a photocatalyst to exhibit excellent chemoselectivity and stability toward aerobic oxidation of structurally diverse and dysfunctional alcohols (20 examples) with dimethyl carbonate as a green reaction solvent. The control experiments with various species scavengers reveal the role of the active species in the photocatalytic system, and the ESR results further confirm O₂^{•−} as the dominate oxidative species for the reaction. Through that the plausible reaction mechanism for the photocatalytic selective oxidation of alcohols over the C/T catalysts is proposed.

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1. Introduction

Catalytic oxidation of alcohols to corresponding aldehydes is an important organic catalytic reaction and is widely applicable to the synthesis of various chemicals [1–4]. Traditionally, taking benzaldehyde as an example, there are two different kinds of synthetic pathways in industrial production. One is obtained by the conventionally chlorination-hydrolysis of toluene or oxidation of toluene [5,6]. The price of obtained product is low but toxic and cancerogenic substance residual (e.g. Cl, F) involved. The other one synthesized by a green pathway can be directly applied to the production of high-grade chemical for its acting as natural cosmetic or medical source, which belongs to the high value-added material [7,8]. However, the low yield for desired products and the high-energy consumption hinder its wider application. Moreover, the low chemo-selectivity or chemical deactivation for particular primary aldehydes with complicated substituent groups, however, is an inevitable bottleneck for achieving industrial application.

Over the past few decades, photocatalysis has been proved to be a potential alternative to conventional catalysis to meet the requirements of sustainable chemistry [9,10]. A great quantity of

works have been endeavoured to explore photocatalyst for selective organic transformations [11–18]. Among these, TiO₂-based photocatalysts have been widely studied [18–25], which show considerable prospect for the selective transformation of alcohols to corresponding aldehydes. Such as they were, the overlook of general applicability for alcohols with high toxic of various organic reaction solvents (e.g. acetonitrile, trifluorotoluene) or catalysts (e.g. CdS, ZnS) in the preparation process inevitably hindered the extending application to a great extent [16,26–28]. In virtue of the modified TiO₂ to construct a complete green catalytic system has attracted much attention, however, the improvement of yield for complicated and dysfunctional aldehydes over the modified TiO₂ in the solvent of water or solvent-free condition under visible light irradiation is still a big challenge [19,25]. Since 1992, dimethyl carbonate (DMC) has been recognized to be a very promising solvent for chemical industry because of its non-toxic, low cost, high-security and excellent solubility [29,30]. It is therefore necessary to explore a high efficiency and green catalytic system based on the photocatalyst and reaction solvent.

We present that carbonate-like species doped TiO₂ (C/T) nanocomposite materials [31] obtained via a mild method can be used as efficient catalysts for aerobic oxidation of various alcohols to aldehydes using DMC as a solvent under visible light irradiation, and through that a green reaction system is achieved. And the photocatalyst is proved to preform better activity than nitrogen-doped

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TiO₂ (N-TiO₂) and commercial P25. Besides, it possesses best photocatalytic property comparing with reported photocatalysts under visible light. And it is noteworthy property for C/T-200 possessing good performance in conversion of alcohols, that is particularly with complicated substituent groups, when DMC is used as solvent.

2. Experimental section

2.1. Sample preparation

The detailed preparation process was discussed in the previous report. Briefly, Titanium isopropoxide, C₃H₈O and CH₃COOH were stirred for 20 h at 323 K, and H₂O was added for hydrolysis for 4 h under ambient air. The suspension was then treated by hydrothermal method maintained at 100 °C for 4 h. After treatment of centrifuging and drying, the as-prepared carbon-doped TiO₂ nanomaterials (marked as C/T) were further calcined in static air at 100, 200, 300, 400 and 500 °C for 3 h, which are labeled by C/T-100, C/T-200, C/T-300, C/T-400 and C/T-500, respectively. The reference of Nitrogen-doped TiO₂ (TiO_{2-x}N_x) photocatalyst was synthesized as a reference by a typical method, [32] and a commercial TiO₂ of P25 (Degussa) was also used.

2.2. Characterizations

The Brunauer-Emmett-Teller (BET) surface areas and nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP2020 analyzer. The transmission electron microscopy (TEM) was measured on FEI Tecnai G2 F20 S-TWIN operated at an accelerating voltage of 200 kV. Electron spin resonance (ESR) signal of the radicals spin-trapped by 5,5-dimethyl-L-pyrroline-N-oxide (DMPO) was determined on a Bruker ESR A300 spectrometer. For detection of O₂^{•−}, catalyst is dispersed in different solvents into which DMPO/benzyl alcohol solution (1:10, v/v) was added. The mixture was oscillated to obtain well-blending suspension. The 300 W Xe arc lamp was used as radiation source (420 nm < λ < 800 nm), the very light source for our photocatalytic selective oxidation of alcohols.

2.3. Evaluation of photocatalytic properties

Photocatalytic selective oxidation of benzyl alcohol (0.1 mmol, Alfa, >99%) was carried out with 16 mg catalyst dissolved in 1.5 mL dimethyl carbonate (DMC, ≥ 99%), which was saturated with O₂ after 5 min with flow rate of 20 mL/min. The mixture solution was sealed in a 20 mL quartz test tube. The suspensions were irradiated by a 300 W Xe arc lamp (PLS-SXE 300, Beijing Perfectlight Co. Ltd.) with combined UV-CUT filters to ensure the irradiation wavelength in range from 420 to 800 nm (420 nm < λ < 800 nm), of which the light source spectrum is shown in Fig. S1. And the system was cooled by fan to maintain the room temperature. The mixture was centrifuged (TDL-5-A) to remove the powders. The filtrates were analysed on Agilent Gas Chromatograph (GC-7890, with a capillary FFAP analysis column). In the photocatalytic stability experiments, the catalysts were recollected by centrifugation and then re-dispersed in DMC solution with benzyl alcohol for next cycle.

3. Results and discussions

The crystalline nature of the material can be characterized by the high-resolution TEM (shown in Fig. 1). And the characteristic crystal fingers of 0.3520 and 0.2378 nm are perfectly indexed as the (101) and (004) crystallographic planes of anatase TiO₂, respectively. Additionally, the blurring of the crystalline (with red arrow in

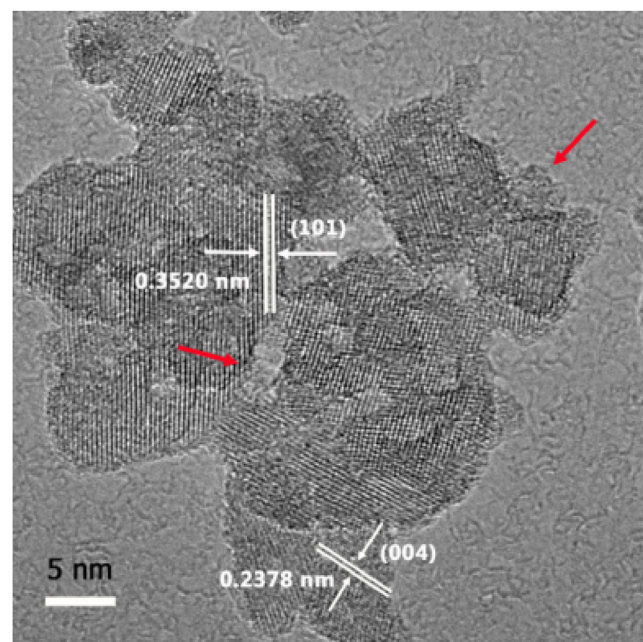


Fig. 1. The high-resolution TEM image of C/T-200.

the figure) may be put down to the coverage of the amorphous carbon. And it may come from the carbonaceous groups on the surface of the TiO₂ particles, which may be favourable to the interaction between the reactant molecular and the bulk TiO₂. Moreover, the role of carbonate species is analysed by Ar etching technique with results in Fig. S2. It is induced that in addition to the surface carbonous species on the TiO₂, the C dopes into the crystal lattice of the TiO₂.

Table 1 presents the photocatalytic performance of various materials for the selective oxidation of benzyl alcohol to benzaldehyde in different conditions. DMC is considered to be stable in the photocatalytic reaction from the analysis result of total organic carbon (TOC) in Table S1. Without catalysts, only 2.5% benzyl alcohol is converted in the DMC solvent. The benzyl alcohol conversion and the selectivity for the desired benzaldehyde over the five kinds of C/T samples were at reasonably high levels (Table 1, entries 2–6). Among them, the C/T-200 possesses the highest conversion of 74.6% for benzyl alcohol, and >99% selectivity for benzaldehyde, and trace of benzoic acid (< 0.1%) is detect over the gas chromatogram shown in Fig. S3. All the C/T catalysts exhibit better photocatalytic performance than P25 and N-TiO₂. P25, which possesses no absorption in the range of visible light, gains non-ignorable conversion. It owes to the visible light absorption after absorbed benzyl alcohol (Fig. S4a), which is due to the formation of a surface complex by the interaction of benzyl alcohol with Ti site [25,33]. And the product of benzaldehyde absorbed on C/T-200 is also believed to make contribution to the origin of visible light responsibility, which can be implied from Fig. S4b and Table S2. To compare the partial oxidation ability of C/T-200 for oxidation of benzyl alcohol to benzaldehyde in DMC with other solvents, the photocatalytic performances in various representative solvents were carried out (entries 3, 9–12). The results indicate that DMC is favourable to acquiring the higher photocatalytic performance than acetonitrile, water and toluene, while slightly lower than that of BTF with the conversion of 80.6%. In other words, besides the superiority of nontoxic and environmental friendly, DMC is an excellent solvent for oxidation of benzyl alcohol over C/T-200. To our knowledge, the polarity of solvents follows the order water > acetonitrile > BTF > DMC > toluene. This indicates that there is no obvious relationship between the polarity of solvents and the catalytic performance (entries 9–12, Table 1). Based on the

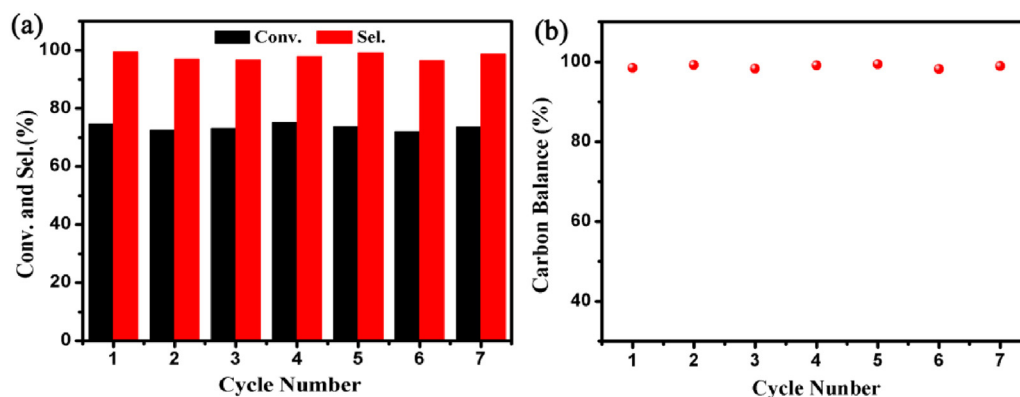


Fig. 2. (a) Recycling test of C/T-200 for selective oxidation of benzyl alcohol to benzaldehyde. (b) Percentage of total organic compounds evolved in solution.

Table 1
Aerobic oxidation of benzyl alcohol by various samples under different conditions.

Entry	Catalyst	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Solvent	Time (h)	Conv. (%)	Sel. (%)
1	–	–	DMC	6	2.5	trace
2	C/T-100	181	DMC	6	71.8	87.5
3	C/T-200	160	DMC	6	74.6	>99
4	C/T-300	128	DMC	6	57.6	>99
5	C/T-400	109	DMC	6	52.6	>99
6	C/T-500	57	DMC	6	47.4	82.5
7	P25	55	DMC	6	12.6	>99
8	N-TiO ₂	135	DMC	6	36.3	94.1
9	C/T-200	160	BTF	6	80.6	>99
10	C/T-200	160	Acetonitrile	6	73.6	>99
11	C/T-200	160	Water	6	51.2	>99
12	C/T-200	160	Toluene	6	61.4	>99

Reaction condition: 16 mg catalyst, 0.1 mmol substrate, 1.5 mL solvent. Light.

Source: 300 W Xe arc-lamp, 420 nm < λ < 800 nm. Desired product: benzaldehyde.

nitrogen adsorption–desorption isotherms in Table 1, it seems that the large surface area is beneficial to the photoactivity. Besides, it possesses best property comparing with reported state-of-the-art photocatalysts under visible light (Table S3). Moreover, the photocatalyst of C/T-200 is considered stable when contrasting the characterizations of C/T-200 before and after reaction (Fig. S5).

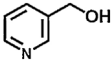

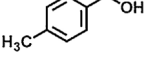
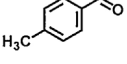
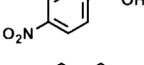
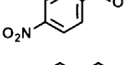
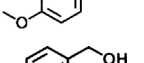
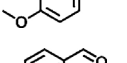
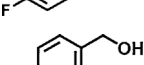
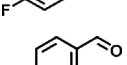
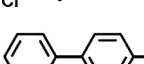
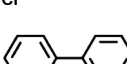
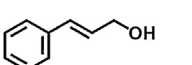
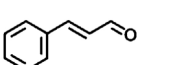
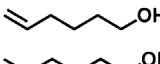
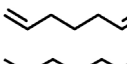
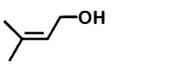
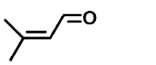
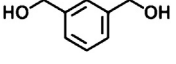
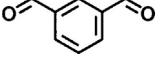
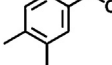
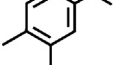
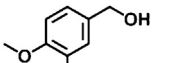
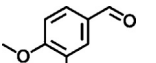
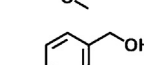
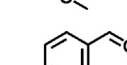
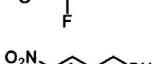
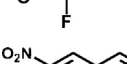
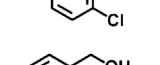
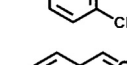
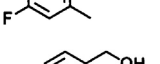
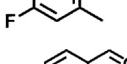
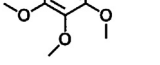
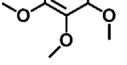
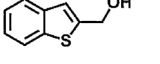
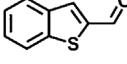
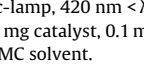
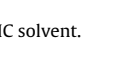
As shown in Fig. 2a, the conversion of benzyl alcohol over C/T-200 is 73.4% along with a benzaldehyde selectivity of 98.5% after seven successive runs, indicating that C/T-200 can be repeatedly used. Carbon balances of each run were verified by taking into account the unreacted alcohol, the produced aldehyde and the trace amounts of acid (Fig. 2b). The carbon balance was quantified as ca. 98% for benzyl alcohol and the small loss may be assigned to the production of open-ring aromatic compounds deriving from overoxidation of aldehyde.

As indicated by the success of benzyl alcohol oxidation, we further applied C/T-200 to a series of alcohols with heterocycle, linear chain, unsaturated, *mono*-, *di*- and *multi*-substituted structures (Table 2). For all these derivatives, there was a reasonable conversion and selectivity output. For instance, 3-pyridinecarboxaldehyde were produced efficiently from 3-pyridinemethanol, and had a conversion of 70.5% and selectivity of 96.5% after eight hours (Table 2, entry 1). The selective oxidation for *para*-substituted alcohols including 4-methylbenzyl alcohol, 4-nitrobenzyl alcohol, 4-methoxybenzyl alcohol, 4-fluorobenzyl alcohol, 4-chlorobenzyl alcohol and 4-biphenylmethanol resulted in 68.4%~95.1% conversion of substrates along with the excellent selectivity for desired products under the optimized reaction conditions (Table 2, entries 2–7). Moreover, some good catalytic performances for the oxidation of unsaturated alcohols, such as cinnamic alcohol, 5-hexen-1-ol, 3-methyl-2-buten-1-ol can be obtained as expected (Table 2, entries 8, 9, 11). Recently, the production of aldehydes

relies on photocatalysts that possess selective aerobic oxidation of alcohol groups in the presence of other easily oxidable functionalities. Here, it was also found that C/T-200 acts as a more potential alternative in the oxidation of *di*- and *tri*- substituted alcohols (Table 2, entries 13–19) including methyl (e.g. 3, 4-dimethylbenzyl alcohol)-, methoxy (e.g. 3, 4-dimethoxybenzyl alcohol, 2,3,4-trimethoxybenzyl alcohol)-, halogen (e.g. 3-fluoro-4-methoxybenzyl alcohol, 4-fluoro-2-methylbenzyl alcohol)-, nitro-groups (e.g. 2-chloro-5-nitrobenzyl alcohol), even in heterocycle substituted alcohol (e.g. 1-benzothiophen-2-ylmethanol). The conversion of alcohols and the selectivity for corresponding aldehydes reach 70.2%~88.2% and 92.1%~99%, respectively. It is found for aromatic alcohols that substituents with electron-withdrawing groups are not conducive to generation of aldehydes, while those with electron-donating groups benefit for the reaction. And it is so consist with the points in other literatures [24,25,34,35]. Moreover, these results also support the notion that electron-donating groups may facilitate to stabilize a radical cation intermediate which could be formed in the transition state of the rate-determining step [24]. Through this way, those aromatic alcohols with electron-donating groups would more easily be photocatalyzed to desired aldehydes. Thus, a cost-effective green catalytic system realizing the selective oxidation of alcohols has been achieved.

In order to study the origin of the photocatalytic performance of C/T-200, the uptakes of various alcohols on catalysts under dark conditions are studied (see Fig. 3). The C/T-200 exhibits the better adsorptivity than that of reference catalysts toward the eight kinds of representative alcohols. And the amount of the surface carbon species is positive related to the adsorption, which is detected by X-ray photoelectron spectroscopy (XPS) with results in Table S4. Moreover, the increased adsorption of C/T-200 in visible light after absorbed benzyl alcohol (Fig. S4a) suggests the contribution of

Table 2
Aerobic oxidation of various substituted alcohols over C/T-200 catalyst^a.

Entry	Substrate	Product	t(h)	Conv. (%)	Sel. (%)
1			8	70.5	96.5
2			6	71.1	>99
3			8	71.5	97.1
4			7	95.1	98.2
5			10	69.5	97.6
6			10	68.4	96.5
7			9	79.9	96.9
8			8	78.5	96.8
9			13	64.5	97.2
10			15	69.5	98.0
11			7	72.9	>99
12			14	81.6	98.5
13			8	80.2	>99
14			12	88.2	95.9
15 ^b			11	72.1	96.3
16 ^b			12	70.2	93.1
17 ^b			10	77.3	94.3
18 ^b			20	84.7	95.2
19 ^b			18	76.9	92.1

Light Source: 300 W Xe arc-lamp, 420 nm < λ < 800 nm.

^a Reaction condition: 12 mg catalyst, 0.1 mmol substrate, 1.5 mL DMC solvent.

^b 20 mg catalyst, 3 mL DMC solvent.

interaction between catalyst and reactant to the light adsorption. These results indicate that the enhanced photocatalytic activity of C/T-200 may be related to the excellent adsorptivity.

Moreover, it was confirmed in our previous work [31] that the bandgap narrowing results in the better photocatalytic activity in visible light, and it is well consistent with that for alcohol conver-

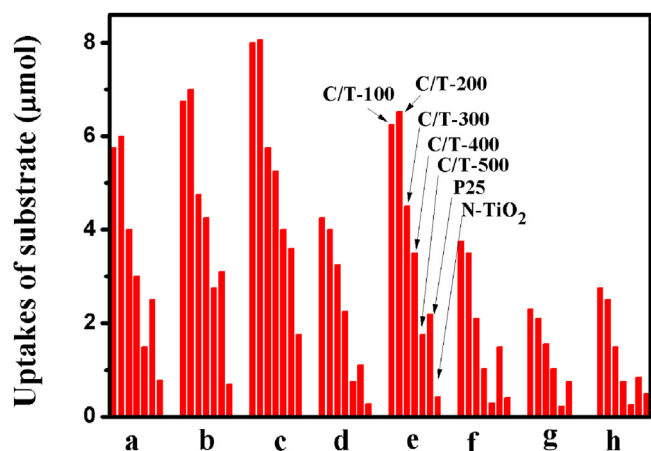


Fig. 3. Uptakes of various alcohols after the adsorption-desorption equilibrium are achieved over various catalysts in the dark: (a) benzyl alcohol; (b) 3-pyridinecarboxaldehyde; (c) 4-methoxybenzyl alcohol; (d) cinnamic alcohol; (e) 5-hexen-1-ol; (f) 3-fluoro-4-methoxybenzyl alcohol; (g) 2,3,4-trimethoxybenzyl alcohol and (h) 1-benzothiophen-2-ylmethanol.

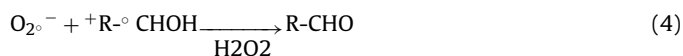
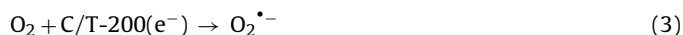
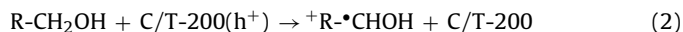
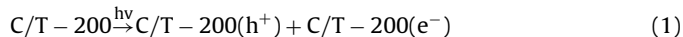
sion over C/T photocatalysts. Hereby, the narrowing of the bandgap is considered playing a dominate role in the partial oxidation of alcohol to corresponding aldehyde.

Electron spin resonance (ESR) was employed to investigate the active oxygen species of the catalysts under simulated experiment conditions. As shown in Fig. 4a, the stronger peaks for DMPO- $O_2^{\bullet-}$ species can be observed over the C/T-200 than that of C/T-100, C/T-300, C/T-400 and C/T-500 catalysts with the present of benzyl alcohol. Compared with some typical reference photocatalysts (P25, N-TiO₂), C/T-200 also exhibited the obvious signal peaks of $O_2^{\bullet-}$ species (see Fig. 4b), suggesting that the $O_2^{\bullet-}$ species is critical to the alcohols oxidation reaction. And the ESR signal of phenoxyl radicals ($^+R\cdot\text{CHOH}$) [36,37] is detected with result in Fig. S6. Moreover, the effects of solvents on the active oxygen species were explored by using ESR. Fig. 5a illustrates that DMC as solvent is more favourable to form the $O_2^{\bullet-}$ species than other solvents and thus facilitates the aerobic oxidation of benzyl alcohol to benzaldehyde. In addition, there is no obvious relationship between the polarity of solvents and the peak intensity of $O_2^{\bullet-}$ species (Fig. 5a).

It is of great importance to detect the main oxidative species in the photocatalytic process for revealing the photocatalytic mechanism. So the comparative experiments using different radical scavengers for the photocatalytic selective oxidation of benzyl alcohol over C/T-200 in the DMC solvent are put into practice with the

results exhibited in Fig. 5b. When BQ (benzoquinone) is added as an active scavenger of $O_2^{\bullet-}$, the conversion decrease the most to 15.2%, suggesting the dominate role of $O_2^{\bullet-}$ in the reaction process. The photogenerated electron may form $O_2^{\bullet-}$ to take part in the oxidation, and AgNO₃ as scavenger for electron is used to determine the effect of it. It is seen from Fig. 5b that the conversion decreases the second to 26.8% when AgNO₃ added. The result further confirms the import effect of $O_2^{\bullet-}$ in the oxidation process. Hole as an import oxidation species in the photocatalytic reaction is trapped by AO (ammonium oxalate), and 46.7% of benzyl alcohol converses to benzaldehyde. Whenas TBA (*tert*-butyl alcohol) as the radical scavenger for hydroxyl radicals is used, still 63.6% conversion obtained, indicating the less contribution of $\cdot\text{OH}$ for the reaction. Considering hole and $\cdot\text{OH}$ of strong and indiscriminately oxidative ability [15,16], the non-dominated roles of hole and $\cdot\text{OH}$ propel the high conversion and selectivity for corresponding aldehydes. And it is concluded that the contribution of the active species for the efficient production of aldehyde follows the order $O_2^{\bullet-} > e^- > h^+ > \cdot\text{OH}$.

From the results above, it is concluded that the $O_2^{\bullet-}$ plays a dominate role in the selective oxidation of alcohols to corresponding aldehydes. The photocatalytic reaction process of the selective oxidation of alcohols can be proposed as follows. Hole and electron are produced when the photocatalyst is excited by the visible light. The hole can directly activate alcohols to form alcohol radicals (Fig. S6). And the electron can trap O_2 to form radical species of $O_2^{\bullet-}$, subsequently it can react with alcohol radicals to form the corresponding aldehydes with removal of H_2O_2 [16], of which the existence is verified from the result in Fig. S7. Furthermore, the benzylic alcohol absorbed on catalyst may form charge-transferred complexes on the surface, and it may result in new photoexcitation pathway from adsorbed benzylic alcohols to TiO₂ conduction band. The tentative reaction mechanism is presented in Scheme 1.



Moreover, the surface abundant oxygen species and trace amorphous carbon may provide an effective platform to adsorb various alcohols, and leading to the reasonable conversion and general applicability. Considering of the similar character of dimethyl carbonate with ammonium oxalate and formation $O_2^{\bullet-}$ of over TiO₂ [38,39], it is surmised that dimethyl carbonate may capture hole

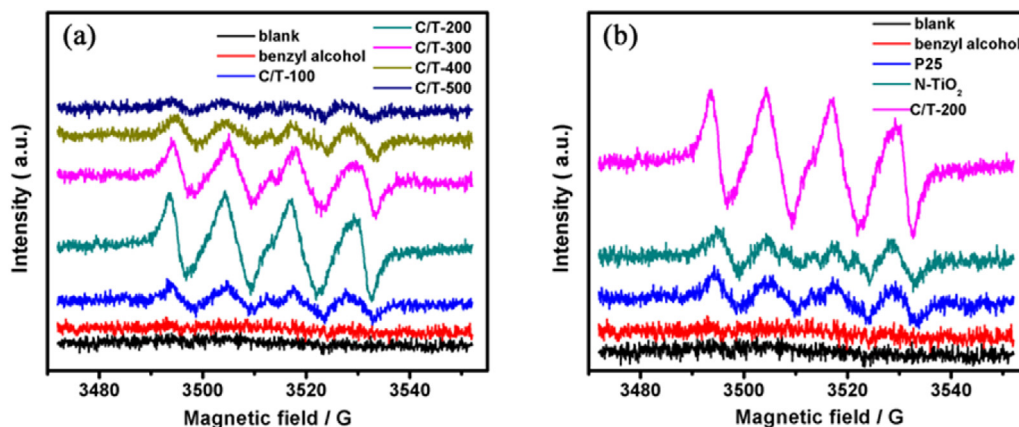


Fig. 4. ESR spectra of $O_2^{\bullet-}$ superoxide radical species trapped by DMPO over C/T series dispersions in DMC solvent (a), and the compared spectra with P25 and N-TiO₂ (b) under the visible light.

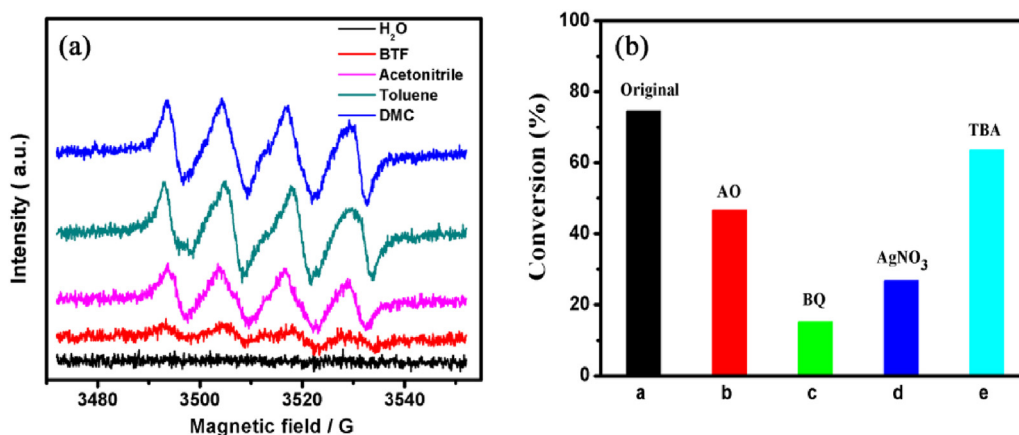
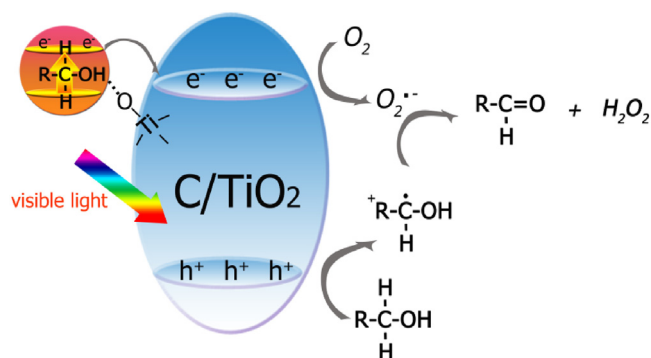


Fig. 5. (a) ESR spectra of $O_2^{\bullet-}$ species trapped by DMPO over C/T-200 dispersions in different solvents under the visible light. (b) Comparative experiments using different radical scavengers for the photocatalytic selective oxidation of benzyl alcohol over C/T-200 in the DMC solvent.



Scheme 1. The proposed mechanism of the photocatalytic selective oxidation of alcohols over C/T-200.

to facilitate the formation of $O_2^{\bullet-}$. The increased quantity of the main active species of $O_2^{\bullet-}$ contributes the enhanced photocatalytic activity of the selective oxidation.

4. Conclusions

In summary, we have developed a potential green catalytic reaction pathway in which C/T-200 as an efficient catalyst exhibiting high conversion (74.6%) and selectivity (>99%) for selective oxidation of alcohols to aldehydes in a mild reaction condition with visible light in solvent of dimethyl carbonate. The dimethyl carbonate is demonstrated to be an ideal solvent for the reaction compared with other solvents. And the catalyst of C/T-200 exhibits high stability over the cycling experiment in this reaction system. Moreover, in the reaction process, $O_2^{\bullet-}$ is found to be the dominate contribution to the selective oxidation of alcohols to corresponding aldehydes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.05.066>.

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